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(54) Aluminosilicate glass for flat panel display.

(57) A flat panel display comprising an aluminosilicate glass panel that exhibits a strain point higher than 640 °C, a weight loss less than 20 mg/cm<sup>2</sup> after immersion for 24 hours in an aqueous 5% by weight HCl solution at 95 °C, a CTE in the range of 31-57x10<sup>-7</sup>/°C, is nominally free of alkali metal oxides and has a composition consisting essentially of, as calculated in percent by weight on an oxide basis, 49-67% SiO<sub>2</sub>, at least 6% Al<sub>2</sub>O<sub>3</sub>, the Al<sub>2</sub>O<sub>3</sub> being 6-14% in conjunction with 55-67% SiO<sub>2</sub> and 16-23% in conjunction with 49-58% SiO<sub>2</sub>, SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> > 68%, 0-15% B<sub>2</sub>O<sub>3</sub>, at least one alkaline earth metal oxide selected from the group consisting of, in the proportions indicated, 0-21% BaO, 0-15% SrO, 0-18% CaO, 0-8% MgO and 12-30% BaO + CaO + SrO + MgO.

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The invention relates to aluminosilicate glass, especially useful for flat panel display device.

#### BACKGROUND OF THE INVENTION

Flat panel displays are of increasing interest, for instance for laptop computers, but also for larger units for information and entertainment applications. One particular form of flat panel display is known as a liquid crystal display.

Liquid crystal displays (LCDs) are flat panel display devices which depend upon external sources of light for illumination.

U. S. Patent No. 4,824,808 (Dumbaugh, Jr.) lists four essential properties for LCD substrate glasses.

First, the glass must be essentially free of intentionally added alkali metal oxide to avoid the possibility that alkali metal from the substrate can migrate into the transistor matrix;

Second, the glass substrate must be sufficiently chemically durable to withstand the reagents used in the TFT matrix deposition process;

Third, the expansion mismatch between the glass and the silicon present in the TFT array must be maintained at a relatively low level even as processing temperatures for the substrates increase; and

Fourth, the glass must be capable of being produced in high quality thin sheet form at low cost; that is, it must not require extensive grinding and polishing to secure the necessary surface finish.

That last requirement is most difficult to achieve inasmuch as it demands a sheet glass production process capable of producing essentially finished glass sheet. Currently, the overflow downdraw sheet manufacturing process is employed. This process is described in U. S. Patent No. 3,338,696 (Dockerty) and U. S. Patent No. 3,682,609 (Dockerty). That process requires a glass exhibiting a very high viscosity at the liquidus temperature plus long term stability, e.g., periods of 30 days, against devitrification at melting and forming temperatures.

Corning Code 7059 glass, supra, is currently employed in the fabrication of LCDs. That glass, consisting essentially, in weight percent, of about 50%  $\text{SiO}_2$ , 15%  $\text{B}_2\text{O}_3$ , 10%  $\text{Al}_2\text{O}_3$ , and 24%  $\text{BaO}$ , is nominally free of alkali metal oxides, and exhibits a linear coefficient of thermal expansion, CTE, ( $25^\circ\text{--}300^\circ\text{C}$ ) of about  $46 \times 10^{-7}/^\circ\text{C}$  and a viscosity at the liquidus temperature in excess of 60,000 Pa·s (600,000 poises). The high liquidus viscosity of the glass enables it to be drawn into sheet via the overflow downdraw sheet processing technique, but its relatively low strain point ( $\sim 593^\circ\text{C}$ ) is adequate only for processing a-Si devices and not for poly-Si devices.

Accordingly, extensive research with insufficient success has been directed at developing glasses designed to meet at least three general requirements, see U.S. Patents 4,409,337; 4,824,808; 5,116,788; and 5,116,789. Initially, the glasses had to be adapted to use in fabricating poly-Si devices. Next, they had to be capable of being formed into sheet by the overflow downdraw process. Finally, they had to have linear CTEs that closely matched silicon.

A recent advance in liquid crystal technology termed "chip-on-glass" (COG) has further emphasized the need for the substrate glass to closely match silicon in thermal expansion. Thus, the initial LCD devices did not have their driver chips mounted on the substrate glass. Instead, the silicon chips were mounted remotely and were connected to the LCD substrate circuitry with compliant or flexible wiring. As LCD device technology improved and as the devices became larger, these flexible mountings became unacceptable, both because of cost and of uncertain reliability. This situation led to Tape Automatic Bonding (TAB) of the silicon chips. In that process the silicon chips and electrical connections to the chips were mounted on a carrier tape, that subassembly was mounted directly on the LCD substrate, and thereafter the connection to the LCD circuitry was completed. TAB decreased cost while improving reliability and increasing the permitted density of the conductors to a pitch of approximately 200  $\mu\text{m}$  -- all significant factors. COG, however, provides further improvement over TAB with respect to those three factors. Hence, as the size and quality requirements of LCD devices increase, COG is demanded for those devices dependent upon the use of integrated circuit silicon chips. For that reason, the substrate glass must demonstrate a linear coefficient of thermal expansion closely matching that of silicon; i.e., the glass must exhibit a linear coefficient of thermal expansion ( $0^\circ\text{--}300^\circ\text{C}$ ) between  $31\text{--}44 \times 10^{-7}/^\circ\text{C}$ , most preferably  $32\text{--}40 \times 10^{-7}/^\circ\text{C}$ .

The high viscosity value at the liquidus required for the overflow downdraw process, 600,000 poises (60,000 Pa·s), has been difficult to obtain in conjunction with the several other properties required for poly-Si devices. Consequently, attention has been given to other sheet-forming processes where the viscosity factor is not of such great significance. These include the float process and a redraw process.

The float process involves drawing a continuous sheet of glass over the surface of a molten metal, such as molten tin. The surface contacting the molten metal is not exposed during drawing, and hence is relatively smooth and free from defects. This has the virtue of requiring Finishing of only one surface. It is a

primary purpose of the present invention to provide panels for flat panel display devices, in particular, LCD devices embodying poly-Si chips. A further purpose is to provide such panels that can be fabricated by a method other than the overflow downdraw process, such as the float process.

## 5 SUMMARY OF THE INVENTION

The present invention resides in an aluminosilicate glass especially useful as a panel for flat panel display, having a strain point higher than  $640^{\circ}\text{C}$ , CTEs in the range of  $31\text{--}57 \times 10^{-7}/^{\circ}\text{C}$ , a weight loss less than  $20 \text{ mg/cm}^2$  after immersion for 24 hours in an aqueous 5% by weight HCl solution at  $95^{\circ}\text{C}$ , that is nominally free from alkali metal oxides and has a composition consisting essentially, calculated in weight percent on the oxide basis, of 49-67%  $\text{SiO}_2$ , at least 6%  $\text{Al}_2\text{O}_3$ , the  $\text{Al}_2\text{O}_3$  being 6-14% in conjunction with 55-67%  $\text{SiO}_2$  and 16-23% in conjunction with 49-58%  $\text{SiO}_2$ ,  $\text{SiO}_2 + \text{Al}_2\text{O}_3 > 68\%$ , 0-15%  $\text{B}_2\text{O}_3$ , at least one alkaline earth metal oxide selected from the group consisting of, in the preparations indicated, 0-21%  $\text{BaO}$ , 0-15%  $\text{SrO}$ , 0-18%  $\text{CaO}$ , 0-8%  $\text{MgO}$  and 12-30%  $\text{BaO} + \text{CaO} + \text{SrO} + \text{MgO}$ .

The method of the invention produces a glass panel for a flat panel display which comprises melting a batch for an aluminosilicate glass consisting essentially of, as calculated in percent by weight on an oxide basis, 49-67%  $\text{SiO}_2$ , at least 6%  $\text{Al}_2\text{O}_3$ , the  $\text{Al}_2\text{O}_3$  being 6-14% in conjunction with 55-67%  $\text{SiO}_2$  and 16-23% in conjunction with 49-58%  $\text{SiO}_2$ ,  $\text{SiO}_2 + \text{Al}_2\text{O}_3 > 68\%$ , 0-15%  $\text{B}_2\text{O}_3$ , at least one alkaline earth metal oxide selected from the group consisting of, in the indicated proportions, 0-21%  $\text{BaO}$ , 0-15%  $\text{SrO}$ , 0-18%  $\text{CaO}$ , 0-8%  $\text{MgO}$  and 12-30%  $\text{BaO} + \text{CaO}$ ,  $\text{SrO} + \text{MgO}$ , and drawing a thin sheet of molten glass from the melt.

The invention also contemplates an aluminosilicate glass exhibiting a strain point higher than  $640^{\circ}\text{C}$ , a weight loss less than  $20 \text{ mg/cm}^2$  after immersion for 24 hours in an aqueous 5% by weight HCl solution at  $95^{\circ}\text{C}$ , a CTE between 31 and  $57 \times 10^{-7}/^{\circ}\text{C}$ , nominally free of alkali metal oxides and having a composition consisting essentially of, as calculated in percent by weight on an oxide basis, 49-67%  $\text{SiO}_2$ , at least 6%  $\text{Al}_2\text{O}_3$ , the  $\text{Al}_2\text{O}_3$  being 6-14% in conjunction with 55-67%  $\text{SiO}_2$  and 16-23% in conjunction with 49-58%  $\text{SiO}_2$ ,  $\text{SiO}_2 + \text{Al}_2\text{O}_3 > 68\%$ , 0-15%  $\text{B}_2\text{O}_3$ , at least one alkaline earth metal oxide selected from the group consisting of, in the proportions indicated, 0-21%  $\text{BaO}$ , 0-15%  $\text{SrO}$ , 0-18%  $\text{CaO}$ , 0-8%  $\text{MgO}$  and 12-30%  $\text{BaO} + \text{CaO} + \text{SrO} + \text{MgO}$ .

## DESCRIPTION OF THE INVENTION

The invention arose from a desire for flat display device panels that could be produced by a method that did not impose the requirement of the overflow downdraw process. In particular, it was desired to avoid the need for the very high viscosity at the liquidus temperature of over  $60,000 \text{ Pa}\cdot\text{s}$  (600,000 poises).

At the same time, certain other requirements must be met, however. These include a glass strain point greater than  $640^{\circ}\text{C}$ , good chemical durability, freedom from alkali metals and a controlled coefficient of thermal expansion (CTE).

We have found that these several requirements may be met by members of a nominally alkali metal-free, aluminosilicate glass family having compositions, calculated on an oxide basis, consisting essentially of 49-67%  $\text{SiO}_2$ , at least 6%  $\text{Al}_2\text{O}_3$ , the  $\text{Al}_2\text{O}_3$  being 6-14%  $\text{Al}_2\text{O}_3$  in conjunction with 55-67%  $\text{SiO}_2$ , and 16-23% in conjunction with 49-58%  $\text{SiO}_2$ ,  $\text{SiO}_2 + \text{Al}_2\text{O}_3 > 68\%$ , 0-15%  $\text{B}_2\text{O}_3$ , at least one alkaline earth metal oxide selected from the group consisting of, in the proportions indicated, of 0-21%  $\text{BaO}$ , 0-15%  $\text{SrO}$ , 0-18%  $\text{CaO}$ , 0-8%  $\text{MgO}$  and 12-30%  $\text{BaO} + \text{SrO} + \text{CaO} + \text{MgO}$ .

Compliance with those specified composition intervals has been found necessary in order to obtain glasses illustrating the desired matrix of chemical, forming, and physical properties, as is demonstrated below.

$\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are the glass-forming oxides. At least 49%  $\text{SiO}_2$  and 6%  $\text{Al}_2\text{O}_3$  are required for this purpose, as well as to provide the desired high strain point. Glass melting tends to become difficult with  $\text{SiO}_2$  contents greater than 67% and  $\text{Al}_2\text{O}_3$  contents greater than 23%.

$\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are also of concern with respect to glass durability. In this respect, however, the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  contents are interdependent. Thus, with  $\text{Al}_2\text{O}_3$  contents in the range of 6-14%, a  $\text{SiO}_2$  content of at least 55%, and preferably at least 60%, is necessary to provide the required chemical durability. With an  $\text{Al}_2\text{O}_3$  content in the range of 16-23%, the  $\text{SiO}_2$  content may be as low as 49% while obtaining adequate durability. The total  $\text{SiO}_2 + \text{Al}_2\text{O}_3$  content should be greater than about 68% to achieve the desired durability.

$\text{B}_2\text{O}_3$  tends to soften the glass, that is, lower the melting temperature and facilitate melting. However, it lowers the strain point and is detrimental to durability, particularly in large amounts. Consequently, the  $\text{B}_2\text{O}_3$

content should not exceed about 15%, and preferably is no more than 8%.

Where silicon chips are to be mounted on the glass, and a CTE of  $31-44 \times 10^{-7}/^{\circ}\text{C}$  is necessary, BaO content is preferably maintained low. Other alkaline earth metal oxides and/or  $\text{Al}_2\text{O}_3$  may be substituted.

In general, the alkaline earth metals increase CTE in this order  $\text{Ba} > \text{Sr} > \text{Ca} > \text{Mg}$  with BaO having the greatest effect and MgO the least.

In addition to the constituents recited above, a variety of optional constituents are also contemplated. These include  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{ZnO}$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{Y}_2\text{O}_3$ . Preferably, these oxides are not present in amounts exceeding about 5% by weight since they tend to increase density and may decrease the strain point. In general, any benefits, such as to refractive index or durability, may be obtained otherwise.

Alkali metals and halides tend to poison liquid crystal fluids, and hence are avoided except as unavoidable impurities.

A commonly accepted measure of chemical durability is weight loss when a glass sample is immersed in a 5% by weight solution of HCl for 24 hours at  $95^{\circ}\text{C}$ . For present purposes, the weight loss must be less than  $20 \text{ mg/cm}^2$ , is preferably below 5, and most preferably below one  $\text{mg/cm}^2$ .

There are two levels of coefficient of thermal expansion (CTE) that are relevant in glass panels for display panels, particularly LCD devices. One level is based on what had become a standard in the trade, Code 7059 glass. That glass has a CTE of  $46 \times 10^{-7}/^{\circ}\text{C}$ , and a CTE range of  $44-57 \times 10^{-7}/^{\circ}\text{C}$  has been considered compatible. Preferably, the range is  $45-50 \times 10^{-7}/^{\circ}\text{C}$ .

We have found two aluminosilicate sub-families A and B that provide CTE values at this level. Glasses having compositions that fall within these sub-families consist essentially of, as calculated in weight percent on an oxide basis:

	A	B
$\text{SiO}_2$	50-57	55-67
$\text{Al}_2\text{O}_3$	16-22	6-14
$\text{B}_2\text{O}_3$	0-5.5	0-7.5
MgO	0.5-3	0-6.5
CaO	1-12.5	0-18.5
SrO	0.5-15	0-15.5
BaO	1-21	1-9.5
$\text{MgO} + \text{CaO} + \text{SrO} + \text{BaO}$	-	16.5-28

The other CTE level is based on a desire to match silicon, thus permitting direct chip attachment. Silicon has a CTE of  $36 \times 10^{-7}/^{\circ}\text{C}$ . Accordingly, a CTE range for glass panels may be  $31-44 \times 10^{-7}/^{\circ}\text{C}$ , preferably  $32-40 \times 10^{-7}/^{\circ}\text{C}$ .

To achieve CTE values within these ranges, we have found two aluminosilicate sub-families C and D that meet the requirement. Glasses having compositions that fall within these sub-families consist essentially of, as calculated in weight percent on an oxide basis:

	C	D
$\text{SiO}_2$	49-58	57-66
$\text{Al}_2\text{O}_3$	17.5-23	8-14
$\text{B}_2\text{O}_3$	0-14.5	0-13
MgO	0-8	0-4.5
CaO	0-9	0-9
SrO	0.4-13.5	0.5-13
BaO	0-21	2-21
$\text{MgO} + \text{CaO} + \text{SrO} + \text{BaO}$	13-28	

In another aspect, the invention contemplates a method of producing panels for LCD devices by melting a glass as described above, forming sheet glass from the melt by such processes as the float process, redrawing or rolling, and cutting the sheet into panel size.

DESCRIPTION OF PREFERRED EMBODIMENTS

Table I reports a number of glass compositions. The compositions are expressed in terms of parts by weight on the oxide basis, illustrating the compositional parameters of the present inventive glasses. The sum of the individual components closely approximates 100, being slightly lower due to omission of a fining agent, such as  $As_2O_3$ . Hence, for all practical purposes, the listed values may be considered to reflect weight percent.

The actual batch materials may comprise the desired oxides. They may also comprise other compounds, which, when melted together with the other batch constituents, will be converted into the desired oxides in the proper proportions. For example,  $CaCO_3$  and  $BaCO_3$  can supply the source of  $CaO$  and  $BaO$ , respectively.

Glass batches based on these compositions were compounded. The batches were tumble mixed together thoroughly to assist in obtaining a homogeneous melt, and then charged into platinum crucibles. After placing lids thereon, the crucibles were introduced into furnaces operating at temperatures of  $1650^\circ C$ . To assure the formation of glasses free from inclusions and cords, a two-step melting practice was undertaken. The batch was first melted for about 16 hours and stirred. It was thereafter poured as a fine stream into a bath of tap water to form finely-divided particles of glass. This process is termed "drigaging" in the glass art. In the second step, the finely-divided glass particles (after drying) were remelted at  $1650^\circ C$  for about four hours. The melts were stirred in both directions, i.e., both clockwise and counterclockwise. The melts were then poured onto steel plates to make glass slabs having the approximate dimensions  $18" \times 6" \times 0.5"$  ( $45.7 \times 15.2 \times 1.3$  cm). Those slabs were then transferred immediately to an annealer operating at about  $725^\circ C$ .

It must be recognized that the above description reflects a laboratory melting procedure only. Thus, the inventive glasses are quite capable of being melted and formed utilizing large scale, commercial glass melting and forming equipment. Where desired, fining agents, such as the oxides of arsenic and antimony, may be added in customary amounts. The small residual remaining in the glass has no substantial effect upon the physical properties of the glass.

Table I also recites measurements of several chemical and physical properties determined on the glasses in accordance with measuring techniques conventional in the glass art. The linear coefficient of thermal expansion (CTE) over the temperature range  $0^\circ$ - $300^\circ C$  is expressed in terms of  $\times 10^{-7}/^\circ C$ . The softening point (S.P.), and the strain point (St.P) are expressed in terms of  $^\circ C$ , and were determined via fiber elongation. The durability (Dur) in HCl was evaluated by determining the weight loss ( $mg/cm^2$ ) after immersion in a bath of aqueous 5% by weight HCl operating at  $95^\circ C$  for 24 hours.

TABLE I

	1	2	3	4	5	6
SiO <sub>2</sub>	65	65.4	50.6	65	55.7	64.7
Al <sub>2</sub> O <sub>3</sub>	8.2	13	22.1	8.1	13.6	8.0
B <sub>2</sub> O <sub>3</sub>	7.8	-	6.0	5.8	5.1	-
MgO	3.1	-	-	0.3	3.0	-
CaO	-	-	-	18	7.1	5.7
SrO	13	0.4	12.8	-	5.2	12.9
BaO	2.2	20.7	8.2	2.2	9.3	7.7
CTE	38.6	38.9	41.3	48.5	46.8	49.4
St.P.	692	810	719	669	662	710
S.P.	1016	985	1003	1093	913	980
Dur.	2.73	0.03	6.65	0.69	0.22	0.01
	7	8	9	10	11	12
SiO <sub>2</sub>	50.3	49.9	65.3	61.2	50.3	50.3
Al <sub>2</sub> O <sub>3</sub>	20.1	21.8	8.0	13.3	21.5	21.7
B <sub>2</sub> O <sub>3</sub>	0.6	-	-	5.5	-	-
MgO	0.6	5.9	5.9	2.9	5.8	3.1
CaO	6.4	0.3	-	8.7	0.6	9.2
SrO	0.4	0.5	12.6	5.9	0.4	13
BaO	20.9	20.5	7.0	2.4	20.2	2.2
CTE	48.7	43.5	44.9	43.4	43.6	51.3
St.P.	734	750	714	674	744	728
S.P.	1008	1013	993	928	1012	972
Dur.	4.9	5.4	0.01	0.07	5	240

Table IA records the same glass compositions but reported in terms of mole percent on the oxide basis.

TABLE IA

	1	2	3	4	5	6
SiO <sub>2</sub>	72.43	80.18	63.56	68.05	64.03	75.05
Al <sub>2</sub> O <sub>3</sub>	5.33	9.38	16.36	5.02	9.20	5.48
B <sub>2</sub> O <sub>3</sub>	7.52	0.00	6.48	5.28	5.04	0.00
MgO	5.16	0.00	0.00	0.39	5.12	0.00
CaO	0.00	0.00	0.00	20.19	8.72	7.09
SrO	8.39	0.28	9.33	0.00	3.49	8.67
BaO	0.97	9.93	4.04	0.90	4.18	3.51
	7	8	9	10	11	12
SiO <sub>2</sub>	63.65	62.03	73.34	61.56	62.46	56.70
Al <sub>2</sub> O <sub>3</sub>	14.96	15.94	5.27	10.57	15.70	14.39
B <sub>2</sub> O <sub>3</sub>	0.67	0.00	0.00	0.00	0.00	0.00
MgO	1.23	11.05	9.90	0.33	10.76	15.59
CaO	8.63	0.42	0.00	18.83	0.81	3.72
SrO	0.27	0.34	8.20	0.00	0.26	8.42
BaO	10.35	9.97	3.09	8.54	9.82	0.95

An examination of the above glasses illustrates the care in composition control that must be exercised in preparing glasses to provide the several properties that characterize the present invention. Thus, compositions 1, 4 and 9 are quite similar, except that 1 has a substantial SrO content, 4 has a substantial CaO content, and 9 omits B<sub>2</sub>O<sub>3</sub> in favor of BaO. The consequence is a continuously higher strain point from

1 to 4 to 9, with 1 being marginally acceptable.

Comparisons also illustrate the effect of various oxide contents on durability. Thus, comparing compositions 11 and 12 indicates that substituting alkaline earth metal oxides has an enormous effect on durability. Also, comparing compositions 1 and 6 suggests the beneficial effect of omitting  $B_2O_3$  in favor of alkaline earth metal oxides.

As noted earlier, a preferred CTE range for glass panels compatible with Code 7059 glass is  $45-50 \times 10^{-7}/^\circ C$ . Glasses in aluminosilicate sub-families A' and B' have CTEs in this range and have compositions consisting essentially of, as calculated in weight percent on an oxide basis:

	A'	B'
SiO <sub>2</sub>	50-57	55-67
Al <sub>2</sub> O <sub>3</sub>	16-20	6-13
B <sub>2</sub> O <sub>3</sub>	0-5.5	0-7.5
MgO	2-2.75	2-6.5
CaO	1-7	0-17.5
SrO	0.5-15	0-14.5
BaO	1-21	2-9.5

TABLE II sets forth exemplary compositions within these sub-families. Compositions 13, 14 and 15 exemplify the A' sub-family, while 16, 17 and 18 exemplify the B' sub-family.

TABLE II

	13	14	15	16	17	18
SiO <sub>2</sub>	56.1	52.9	53.7	65.5	56.6	66.9
Al <sub>2</sub> O <sub>3</sub>	17.0	18.2	18.0	8.1	11.2	6.1
B <sub>2</sub> O <sub>3</sub>	-	2.0	4.7	-	7.4	-
MgO	2.3	2.4	2.4	6.1	2.2	6.2
CaO	6.8	6.9	6.5	5.2	2.1	-
SrO	5	5.1	5.1	12.9	12.0	13.3
BaO	12.9	12.6	9.6	2.2	8.7	7.5
CTE	48.3	48.4	45.3	48.1	47.3	45.5
Strain	718	695	677	693	650	699
HCl	0.08	0.62	1.9	0.03	0.3	0.01
Density	2.31	2.80	2.70	2.70	2.72	2.73

Preferred CTE ranges for glass panels adapted to use with silicon have been noted as having a CTE range of  $32-40 \times 10^{-7}/^\circ C$ . Glasses in aluminosilicate sub-families C' and D' have CTEs within that range and have compositions that consist essentially of, as calculated in weight percent on an oxide basis:

	C'	D'
SiO <sub>2</sub>	54-57	57-65.5
Al <sub>2</sub> O <sub>3</sub>	17.5-23	8-13
B <sub>2</sub> O <sub>3</sub>	5-15	4-13
MgO	2-2.75	2-3.5
CaO	1.5-7	0-6.5
SrO	2-6	0-13
BaO	0.5-9.5	2-21

TABLE III sets forth exemplary compositions within these sub-families. The C' sub-family is exemplified by compositions 19, 20 and 21, while the D' sub-family is exemplified by compositions 22, 23 and 24.

TABLE III

	19	20	21	22	23	24
SiO <sub>2</sub>	56.6	55.5	56.2	64.6	65	64.3
Al <sub>2</sub> O <sub>3</sub>	22.4	18.4	22.9	12.9	8.2	13
B <sub>2</sub> O <sub>3</sub>	7.8	9.3	5.9	4.4	7.8	4.4
MgO	2.3	2.3	2.4	2.2	3.1	2.2
CaO	3.4	6.9	4.9	6.3	-	6.3
SrO	4.9	5.0	5.0	0.8	13	1.2
BaO	2.6	2.6	2.7	8.8	2.2	8.7
CTE	32.2	40	35.4	38.8	38.6	38.8
Strain	692	666	706	683	692	686
HCl	1.8	2.6	0.8	0.02	2.7	0.02
Density	2.52	2.54	2.56	2.55	2.54	2.56

In a preferred embodiment of the invention, a glass panel for a flat panel display has a strain point greater than 660 °C and has a weight loss less than 1 mg/cm<sup>2</sup> in the HCl test described earlier. We have found that glasses having compositions falling within two aluminosilicate sub-families meet these preferred qualifications. The two families, E and F, have compositions consisting essentially of, as calculated in weight percent on an oxide basis:

	E	F
SiO <sub>2</sub>	54-58	55-67
Al <sub>2</sub> O <sub>3</sub>	16-23	6-14
B <sub>2</sub> O <sub>3</sub>	0-6	0-7.5
MgO	2-4.5	0-7
CaO	1-12.5	0-18.5
SrO	2.5-15.5	0-15
BaO	0-14.5	1-21
MgO + CaO + SrO + BaO	15-27	18-28

TABLES IVE and IVF set forth, in approximate weight percent as analyzed on an oxide basis, the compositions and relevant properties of several representative examples of each sub-family, respectively:

TABLE IVE

	25	26	27	28	29	30
SiO <sub>2</sub>	55.16	56.95	56.7	57.63	58.19	54.69
Al <sub>2</sub> O <sub>3</sub>	18.19	16.81	22.63	19.21	19.43	17.79
B <sub>2</sub> O <sub>3</sub>	0.95	0	0.997	5.33	5.35	0.94
MgO	2.23	2.25	2.31	2.6	2.67	2.17
CaO	1.46	4.7	6.7	8.63	8.76	1.39
SrO	13.06	4.82	4.86	5.5	5.61	14.25
BaO	8.94	14.47	5.77	1.09	0	8.76
CTE	45.4	46.8	41.8	42	41	46.8
Strain	731	724	748	684	688	722
HCl	0.074	0.06	0.57	0.16	0.48	0.11
Density	2.79	2.429	2.676	2.579	2.564	2.819

TABLE IVF

	31	32	33	34	35	36
SiO <sub>2</sub>	55.7	55.53	56.9	65.49	66.93	66.85
Al <sub>2</sub> O <sub>3</sub>	13.6	13.3	13.03	8.14	6.1	6.23
B <sub>2</sub> O <sub>3</sub>	5.1	3.2	7.3	0	0	0
MgO	3	2.27	2.2	6.08	6.23	0.13
CaO	7.1	4.08	0	5.16	0	5.69
SrO	5.2	12.59	11.9	12.92	13.26	13.29
BaO	9.3	9.03	8.7	2.22	7.48	7.8
CTE	46.8	50.2	45	48.1	45.5	50.9
Strain	662	675	662	693	699	699
HCl	0.22	0.076	0.31	0.03	0.0134	0.0058
Density	2.705	2.799	2.692	2.695	2.725	2.741

A further preferred embodiment constitutes glass panels having a density less than 2.5 grams/cc. Glasses meeting this requirement fall within an aluminosilicate sub-family G having the following constituent ranges consisting essentially of, as analyzed on an oxide basis:

SiO <sub>2</sub>	54.8-57
Al <sub>2</sub> O <sub>3</sub>	16.8-21.8
B <sub>2</sub> O <sub>3</sub>	0-14
MgO	2.2-2.5
CaO	1.5-9.5
SrO	4.5-5.5
BaO	0.1-14.5
MgO + CaO + SrO + BaO	12.5-27

TABLE V sets forth in approximate weight percent, as analyzed on an oxide basis, compositions and relevant properties for representative examples:

TABLE V

	37	38	39	40	41	42
SiO <sub>2</sub>	55.9	56.08	56.95	56.14	56.6	56.72
Al <sub>2</sub> O <sub>3</sub>	21.73	16.98	16.81	21.1	16.92	19.04
B <sub>2</sub> O <sub>3</sub>	9.76	0	0	1.06	0.99	9.73
MgO	2.45	2.28	2.25	2.28	2.31	2.37
CaO	2.36	6.78	4.7	5.59	9.4	6.95
SrO	5.13	5	4.82	4.84	4.78	5.07
BaO	2.67	12.86	14.47	8.99	8.91	0.12
CTE	31.2	48.3	46.8	43.6	49.3	37.6
Strain	680	718	724	737	710	670
HCl	3.36	0.08	0.06	0.27	0.15	4.15
Density	2.496	2.312	2.429	2.467	2.265	2.494

Further exemplary working embodiments of the invention are:  
an aluminosilicate glass which has a CTE of  $32-40 \times 10^{-7}/^{\circ}\text{C}$  and the aluminosilicate sub-families consist essentially of:

a. 54-57% SiO<sub>2</sub>, 17.5-23% Al<sub>2</sub>O<sub>3</sub>, 5-15% B<sub>2</sub>O<sub>3</sub>, 2-2.75% MgO, 1.5-7% CaO, 2-6% SrO and 0.5-9.5% BaO,

b. 57-65.5% SiO<sub>2</sub>, 8-13% Al<sub>2</sub>O<sub>3</sub>, 4-13% B<sub>2</sub>O<sub>3</sub>, 2-3.5% MgO, 0-6.5% CaO, 0-13% SrO and 2-21% BaO.  
an aluminosilicate glass which glass has a CTE in the range of  $45-50 \times 10^{-7}/^{\circ}\text{C}$  and the aluminosilicate sub-families consist essentially of:

- a. 50-57% SiO<sub>2</sub>, 16-20% Al<sub>2</sub>O<sub>3</sub>, 0-5.5% B<sub>2</sub>O<sub>3</sub>, 2-2.75% MgO, 1-7% CaO, 0.5-15% SrO and 1-21% BaO,
- b. 55-67% SiO<sub>2</sub>, 6-13% Al<sub>2</sub>O<sub>3</sub>, 0-7.5% B<sub>2</sub>O<sub>3</sub>, 2-6.5% MgO, 0-17.5% CaO, 0-14.5% SrO and 2-9.5% BaO.

# Claims

1. An aluminosilicate glass exhibiting a strain point higher than 640 °C, a weight loss less than 20 mg/cm<sup>2</sup> after immersion for 24 hours in an aqueous 5% by weight HCl solution at 95 °C, a CTE between 31 and 57x10<sup>-7</sup>/°C, nominally free of alkali metal oxides and having a composition consisting essentially of, as calculated in percent by weight on an oxide basis, 49-67% SiO<sub>2</sub>, at least 6% Al<sub>2</sub>O<sub>3</sub>, the Al<sub>2</sub>O<sub>3</sub> being 6-14% in conjunction with 55-67% SiO<sub>2</sub> and 16-23% in conjunction with 49-58% SiO<sub>2</sub>, SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> > 68%, 0-15% B<sub>2</sub>O<sub>3</sub>, at least one alkaline earth metal oxide selected from the group consisting of, in the proportions indicated, 0-21% BaO, 0-15% SrO, 0-18% CaO, 0-8% MgO and 12-30% BaO + CaO + SrO + MgO.
2. An aluminosilicate glass in accordance with claim 1 having a CTE in the range of 31-44x10<sup>-7</sup>/°C and being selected from a group of aluminosilicate sub-families consisting of glasses having compositions consisting essentially of, as calculated in weight percent on an oxide basis:
  - a. 49-58% SiO<sub>2</sub>, 17.5-23% Al<sub>2</sub>O<sub>3</sub>, 0-14.5% B<sub>2</sub>O<sub>3</sub>, 0-8% MgO, 0-9% CaO, 0.4-13.5% SrO, 0-21% BaO, the glass containing at least one alkaline earth oxide in the indicated proportion and the total BaO + CaO + SrO + MgO content being 13-28%.
  - b. 57-66% SiO<sub>2</sub>, 8-14% Al<sub>2</sub>O<sub>3</sub>, 0-13% B<sub>2</sub>O<sub>3</sub>, 0-4.5% MgO, 0-9% CaO, 0.5-13% SrO, 2-21% BaO.
3. An aluminosilicate glass in accordance with claim 1 having a CTE in the range of 44-57x10<sup>-7</sup>/°C and being selected from a group of aluminosilicate sub-families consisting of glasses having compositions consisting essentially of, as calculated in weight percent on an oxide basis:
  - a. 50-57% SiO<sub>2</sub>, 16-22% Al<sub>2</sub>O<sub>3</sub>, 0-5.5% B<sub>2</sub>O<sub>3</sub>, 0.5-3% MgO, 1-12.5% CaO, 0.5-15% SrO, 1-21% BaO,
  - b. 55-67% SiO<sub>2</sub>, 6-14% Al<sub>2</sub>O<sub>3</sub>, 0-7.5% B<sub>2</sub>O<sub>3</sub>, 0-6.5% MgO, 0-18.5% CaO, 0-15.5% SrO, 1-9.5% BaO, the total MgO + CaO + SrO + BaO being 16.5-28%.
4. An aluminosilicate glass in accordance with claim 1 having a strain point greater than 660 °C and a weight loss less than 1 mg/cm<sup>2</sup> after immersion for 24 hours in an aqueous 5% by weight HCl solution at 95 °C and being selected from a group of aluminosilicate sub-families consisting of glasses having compositions consisting essentially of, as calculated in percent by weight on an oxide basis:
  - a. 54-58% SiO<sub>2</sub>, 16-23% Al<sub>2</sub>O<sub>3</sub>, 0-6% B<sub>2</sub>O<sub>3</sub>, 2-4.5% MgO, 1-12.5% CaO, 2.5-15.5% SrO and 0-14.5% BaO, MgO + CaO + SrO + BaO being 15-27%.
  - b. 55-67% SiO<sub>2</sub>, 6-14% Al<sub>2</sub>O<sub>3</sub>, 0-7.5% B<sub>2</sub>O<sub>3</sub>, 0-7% MgO, 0-18.5% CaO, 0-15% SrO, 1-21% BaO, MgO + CaO + SrO + BaO being 18-28%.
5. An aluminosilicate glass in accordance with claim 1 having a density less than 2.5 grams/cc and a composition consisting essentially of 54.8-57% SiO<sub>2</sub>, 16.8-21.8% Al<sub>2</sub>O<sub>3</sub>, 0-14% B<sub>2</sub>O<sub>3</sub>, 2.2-2.5% MgO, 1.5-9.5% CaO, 4.5-5.5% SrO, 0.1-14.5% BaO, MgO + CaO + SrO + BaO being 12.5-27%.

(19)



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(54) **Aluminosilicate glass for flat panel display**

(57) A flat panel display comprising an aluminosilicate glass panel that exhibits a strain point higher than 640°C, a weight loss less than 20 mg/cm<sup>2</sup> after immersion for 24 hours in an aqueous 5% by weight HCl solution at 95°C, a CTE in the range of 31-57x10<sup>-7</sup>/°C, is nominally free of alkali metal oxides and has a composition consisting essentially of, as calculated in percent by weight on an oxide basis, 49-67% SiO<sub>2</sub>, at least 6% Al<sub>2</sub>O<sub>3</sub>, the Al<sub>2</sub>O<sub>3</sub> being 6-14% in conjunction with 55-67% SiO<sub>2</sub> and 16-23% in conjunction with 49-58% SiO<sub>2</sub>, SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub> > 68%, 0-15% B<sub>2</sub>O<sub>3</sub>, at least one alkaline earth metal oxide selected from the group consisting of, in the proportions indicated, 0-21% BaO, 0-15% SrO, 0-18% CaO, 0-8% MgO and 12-30% BaO+CaO+SrO+MgO.

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## EUROPEAN SEARCH REPORT

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The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 22 May 1996	Examiner Kuehne, H-C
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# EUROPEAN SEARCH REPORT

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The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 22 May 1996	Examiner Kuehne, H-C
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>----- &amp; : member of the same patent family, corresponding document</p>			

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